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Gelatinized and nongelatinized starch/pp blends: effect of starch source and carboxylic and incorporation

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Abstract

Due to the environmental impact caused by incorrect disposal and the non-biodegradability of synthetic polymers, the packaging sector seeks renewable raw materials. An alternative is the utilization of natural renewable polymer, such as thermoplastic starch (TPS), mixed with synthetics. However, the chemical incompatibility between these two materials leads to the use of a compatibilizer agent. Even though the compatibilizer effect of carboxylic acid on TPS blends have been studied, the correlation between the carboxylic acid and the starch source has not been investigated yet. Thus, this study focuses on the effects of added carboxylic acids (myristic (C14) and stearic (C18) acid) and the starch sources (corn, cassava, and potato) on the properties and microstructure of blends with TPS/PP (70/30). The results suggested that the compatibilizer effect of acids depends on the starch source and the length of the acid chain, where cassava blends with C14 showed better results. Acid insertion increased tensile strength and deformation at break, but reduced the elastic modulus, indicating a plasticizer effect. This behavior was related to the formation of amylose and lipid complexes (endogenous or added) during heating. Torque reduction and Tg displacement were also observed for acid blends. The SEM images showed two different morphological dispersions and a non-gelatinization effect due to the acid insertion. Results suggested that acids act differently according to the starch source.

Keywords Starch source · Carboxylic acid · Blends · Properties · Compatibility

Introduction

Over the last few years, there was an increasing interest in polymers made from renewable sources, such as starch. Starch is considered a natural polymer because it is a polysaccharide and consists of numerous glucose units linked by glycoside bonds. Two macromolecules with different molar masses and structures make up their structure: amylose and amylopectin. Amylose is formed by a linear structure with α-1,4-D-glucose units, exhibiting behavior similar to the conventional polymers, whereas amylopectin is highly branched with α-1,4 and α-1,6 D-glucose units [1, 2].

Starch without plasticizers gives rise to fragile and brittle materials, with melting temperature greater than the degradation temperature. Due to the strong intermolecular interactions, the starch undergoes decomposition before melting, making it difficult to use in some temperature ranges in the processing. However, this can be improved upon the disruption of the granule which occurs when the starch granules are heated in the presence of a plasticizer, such as water, glycerol or polyvinyl alcohol (PVA) [3–5]. This thermoplastic starch is well-known as TPS [6].

Since starch granules size and amylose/amylopectin content vary with its botanical source, so do its properties [7–10]. Therefore, the starch used can interfere directly in the polymer properties. For example, it was study the characteristics of different starches from non-main stream sources available in China [11]. The authors found that the isolated starches present differences in their morphologies, granule

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size, swelling power, solubility, crystallinity, thermal and adhesive characteristics depending upon their botanical origin. In a study with more evident technological application, it has been shown that that the corn TPS foams presented higher tensile strength than potato and cassava TPS foams [12]. Like pure starch materials, starch blends properties are also affected by starch source. Amylose/amylopectin content can influence on the photodegradation [13], water absorption capacity [14], anaerobic biodegradation [15] of starch-based polymers.

Natural polymers are available in large quantities; however, their use is limited due to some drawbacks like mechanical properties and water absorption. An alternative is to mix them with synthetic and natural polymers [16]. Polymeric blends of polypropylene (PP) and TPS are mechanically resistant and can be applied in various industrial sectors, such as food packaging. In this sense, studies are being conducted to prepare new thermoplastic materials obtained from these blends [17–21]. Furthermore, starch is considered a sustainable biobased product. It is cheap and made from a renewable resource, so the TPS/PP (70/30) blends could be considered as a biobased material [14]. Biobased polymers hold the potential to reduce dependence on fossil-based carbon source, and to provide polymers offering a lower environmental burden.

Nevertheless, there was an obstacle to make PP/TPS blends. The chemical incompatibility between hydrophilic TPS and the hydrophobic PP, which worsens the mechanical properties. To overcome this issue, some polyolefin grafted with maleic anhydride (MA) is widely used [22–24]. However, MA is expensive, difficult to manufacture and like petroleum-based polymers, non-biodegradable. In order to work around this issue, an alternative is the use of carboxylic acids as natural compatibilizer agents [25, 26]. Carboxylic acids contain a large carbonic chain, which provides the molecular interaction with PP. On the other hand, the carboxylic group is polar and interacts with the hydroxyl groups of TPS. Hu et al.(2020) [27] incorporated carboxylic acids to a polyurethane matrix. This study showed an increase on adhesion between the polar coating and the polyurethane matrix, due to the insertion of acids polar groups (hydroxyls). In this way, the carboxylic acid is positioned at the interface between the PP and the TPS and improves the adhesion between them during the mixture processing.

Myristic acid (C14) and stearic acid (C18) are natural carboxylic acids, which are derived from nutmeg oil and from cacao bean respectively. They are used as ingredient in the food industry [28] and could be obtained from renewable and biodegradable sources. On the other hand, Mohamed et al. (2020) [29], used carboxylic acids in an N-doped porous carbon material, a porous organic polymer, aiming to enhance CO_2 capture. Hazer et al.(2019) [30] used carboxylic acids to functionalized trithiocarbonate, in order to

obtain an amphiphilic copolymer. With the specific purpose of compatibilization, in others works [31, 32], stearic acid was grafted into cassava starch chain. However, to obtain this compound, other reagents and several synthesis and purification steps were used, increasing the energy expenditure involved, as well as increasing the chemical residues.

In order to extend the utilization of carboxylic acid on TPS blends, in the present work, we present an investigation about the interactions among the added carboxylic acids (myristic (C14) and stearic (C18) acid) and the starch source (corn, cassava, and potato) on the properties and microstructure of TPS/PP (70/30) blends.

Materials and methods

Materials

Polypropylene (PP) with melt flow index of 3.3 g/10 min, designed for disposable packaging, was supplied by BRASKEM. Corn (Maizena®), cassava and potato (Foco Alternativo®) starches (food grade) were purchased at a local store in the city of Porto Alegre, RS, Brazil. Carboxylic acids used as natural compatibilizer agents (NCA) were myristic (C14) and stearic (C18) acids, supplied by Dinamica Contemporary Chemistry Ltd.

Amylose content

Starches were analyzed for amylose content following the procedure of [33, 34]. Spectrophotometer measurements (T80 + UV/VIS Spectrometer PG Instruments) were made at 620 nm. A blank sample (with 2 ml of iodine solution and 1 ml of HCl 1 N) was used as standard.

Material processing

Starches were pre-mixed manually with 30 wt% of glycerol until reached a homogeneous mixture and stored at 60 °C for 24 h. Each mixture was processed with PP, with or without acids. An internal mixer (Thermo Scientific Haake Rheomix OS) was used at constant speed of 60 rpm at 165 °C for 7 min. For each starch source, three blends were prepared: control (without acid), 3% C14 and 3% C18 (with 3% of acid per gram of TPS and PP). The ratio of TPS/PP (70/30) was held constant.

Torque and temperature curves were recorded over processing time in order to evaluate the flow behavior of the mixture. The area under the curve is related to the energy absorbed by the material during processing. Specific mechanical energy (SME) required for the processing of each sample was calculated according to Eq. 1.

$$SME = 2\pi N/m \int C(t)dt \qquad (1)$$

where N is the rotation speed (rpm), m is the total sample mass (g), t is the processing time (min) and $C(t)$ is the total torque produced during the processing time (Nm). The SME was expressed in kJ/kg [4, 35].

After mixing, samples were ground in a RETSCH mill using a 1 mm sieve. The material was then oven dried at 60 °C for 24 h and molded by a Thermo Scientific MiniJet II injector at a temperature of 190 °C, mold heated at 50 °C and injection pressure of 350 bar for the preparation of each specimen.

Mechanical tests

The tensile properties were determined using an Instron universal testing machine (EMIC-23-5D) equipped with a load cell of 5 kN. Force (N) and deformation (mm) were recorded using an extension rate of 10 mm/min, with initial distance between the grips equal to 50 mm. The samples were prepared according to the ISO 527 standard, type 5A. The mean value obtained from five samples was reported with standard deviation.

The Izod impact test of the unnotched specimens were conducted using a CEAST- IMPACTOR II equipment, according to ASTM D4812, with a 2.75 J hammer. The samples dimensions were $63.5 \times 12.5 \times 3.3$ mm. Seven measurements were made for each sample and the result obtained corresponds to the mean of the values.

Scanning electron microscopy (SEM) analysis

SEM analyses were performed with a JEOL JSM 6510LV electron microscope. Fracture surfaces of impact test were coated with a thin layer of gold. All samples were examined using an accelerating voltage of 10 kV in the secondary electron mode of operation.

Differential scanning calorimeter (DSC)

Differential scanning calorimetry (DSC) thermograms were recorded by a PerkinElmer equipament. The samples (10 mg) were placed in an aluminum pan and were scanned from room temperature to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The degree of crystallinity of TPS/PP blends was calculated using the following equation:

$$Xc(\%Crystallinity) = \frac{\Delta H_f}{w \times \Delta H_f^\circ} \times 100$$

where ΔH_f is the heat of fusion for PP in the sample, ΔH_f° is the heat of fusion of 100% crystalline PP which is 209 J/g (theorical melting enthalpy) and w is the weight fraction of PP in the blend.

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were determined using a dynamic thermo-mechanical analyzer Mettler Toleto DMA 1 Star System. Injected samples were cut to get specimens with dimensions $19.68 \times 8.70 \times 1.97$ mm. The displacement amplitude was set to 20 μm and the frequency was 1 Hz. The range of temperature was from -80 to 110 °C at a scanning rate of 5 °C min^{-1}.

Statistical analysis

A commercial statistic software was used for all statistical analysis. Means, standard deviation and Tukey test for means comparison were applied. The significance level used was 0.05.

Results and discussion

Influence of starch and acid molecular structure on the mechanical properties of TPS/PP blends.

It can be inferred from the data presented in Fig. 1 that the Izod impact strength for control blends (without acid) was not influenced by starch source and ranged between 4 – 5 kJ/m^2. Although the literature showed that starch origin affect the mechanical properties [12, 15], in these three cases it was not effectively observed. Probably, it was due to the incompatibility between phases and its consequent inability
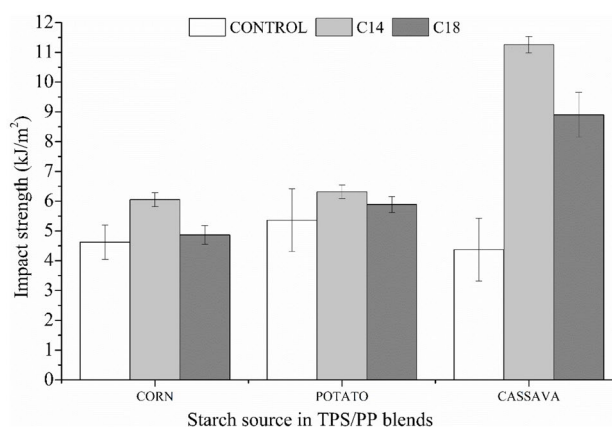
Fig. 1 Impact energy of TPS/PP blends according to starch source for blends without acid (CONTROL), with myristic acid (C14) and stearic acid (C18)

of either starch to support impact strength transfer from PP matrix phase.

On the other hand, after acid incorporation, the impact energy of blends ranged between 5.2 – 11.3 kJ/m², differing from starch source and acid type. Cassava blends with C14 and C18 showed an increase on impact energy of 157% and 103%, respectively, when compared to the control blends. Whereas, corn blends with C14 showed 30% of increase, while corn blends with C18 and potato blends with acids did not exhibit increase. The compatibilizer effect of carboxylic acids on PP/TPS (70/30) blends and its positive effect on impact strength were also demonstrated in a previous work [36]. It was also observed that, among the acids, the shortest carbon chain length (C14) gave rise to blends with better performance. Therefore, impact results suggested that the compatibilizer effect of carboxylic acids depends of starch source and its chain length. It was possible to note a significant difference in the increment between corn and cassava-based blends, where cassava starch and PP matrix seem to have a better interaction through acid incorporation.

Regarding potato starch, potato blends impact strength was not influenced by acid incorporation. This response may be related to potato's grain size. As reported, potato starch is moderately larger in size [11]. Since agglomeration can induces crack propagation, bigger grains also could collaborate for impact strength decrease, since stress transfer is compromised [37].

Tensile properties parameters analysed of all TPS/PP (70/30) blends are present in Table 1. The stress–strain curves of the corn, potato and cassava control blends are shown in Fig. 2a. It is observed that starch source affected significantly tensile strength properties of blends. Corn and potato control blends showed a less flexible behaviour since presented higher elastic modulus and less elongation at break, when compared to cassava control blends.

PP and TPS content were maintained constant, being the starch source the only difference between control blends. One of the main differences between starch sources is the amylose content. This property influence the mechanical properties of starch-based materials [38]. Thus, amylose content test was performed.

Between studied starches, potato starch presented an amylose content of 24.73% ($\pm$0.09), followed by corn starch with 23.09% ($\pm$0.27) and cassava starch 20.39% ($\pm$0.03), all samples were statically different according to Tukey test ($p < 0.05$). Mishra et al. [39], also observed lower amylose content in tapioca (cassava) than potato and corn starches. A higher amylose content on corn and potato starch could explain the brittle behaviour of these blends. Cooling of extruded plasticized samples is usually associated with the conversion from an amorphous to a crystalline form. This phenomenon is called retrogradation and involves the reassociation of long linear amylose chain, increasing crystallinity and consequently the stiffness, but it did not significantly affect tenacity [38, 40]. The tenacity values between control samples did not show a significant difference, which agrees with the impact results.

Acid introduction led to a decrease of elastic modulus and tensile strength at maximum load when compared to control blends (Fig. 2). This could be related to the formation of complexes amylose and lipids (endogenous or added) complexes during heating [41]. When amylose is in a helical conformation it could form: (i) a hydrophilic exterior with active amylose hydroxyl groups and acid carboxyl groups enabling adjacent molecules to interact through hydrogen bonding enhancing the plasticization effect; and (ii) a hydrophobic cavity, which enables interactions with hydrophobic compounds to form starch-inclusion complexes [42]. Analogously, less brittle materials were obtained by Khanoonkon et al. [31] through stearic acid incorporation on starch films and starch blends with LLDPE. Rocca-Smith et al. [43] showed that lipid addition clearly influenced the structure of wheat based films as shown by the decrease in elastic modulus and tensile strength. Thakur et al. [44] showed that mechanical properties are dependent on the complexing of amylose with hydrophobic ligands.

Table 1 Tensile strength properties of all studied TPS/PP (70/30) blends, were E is elastic modulus (MPa), σ_{max} is tensile strength at maximum load (MPa), σ_b is tensile strength at break, ε_b is tensile strain at break (%) and T is tenacity (J)

Starch		E	σ_{max}	σ_b	ε_b	T
CORN	Control	1705[d]$\pm$129	28.13[f]$\pm$1.34	23.24[f]$\pm$0.90	3.0[a]$\pm$0.40	0.24[a]$\pm$0.04
	C14	1386[c]$\pm$143	20.46[d]$\pm$0.33	19.44[e]$\pm$0.38	4.51[b]$\pm$0.31	0.26[a]$\pm$0.05
	C18	1365[c]$\pm$102	20.47[d]$\pm$0.63	19.86[e]$\pm$0.72	4.05[ab]$\pm$0.37	0.24[a]$\pm$0.08
POTATO	Control	1914[e]$\pm$31	26.60[e]$\pm$1.68	18.84[e]$\pm$2.33	2.84[a]$\pm$0.75	0.20[a]$\pm$0.06
	C14	1307[c]$\pm$58	12.98[a]$\pm$0.55	10.36[a]$\pm$0.83	9.25[d]$\pm$2.25	0.43[b]$\pm$0.10
	C18	1344[c]$\pm$31	13.77[a]$\pm$0.46	13.36[b]$\pm$0.38	11.4[e]$\pm$2.02	0.63[c]$\pm$0.06
CASSAVA	Control	1441[c]$\pm$117	18.59[c]$\pm$1.48	15.27[cd]$\pm$1.10	4.13[ab]$\pm$0.63	0.24[a]$\pm$0.04
	C14	952[a]$\pm$54	15.87[b]$\pm$0.65	15.31[d]$\pm$0.70	6.33[c]$\pm$0.84	0.36[b]$\pm$0.07
	C18	1153[b]$\pm$45	14.93[b]$\pm$0.27	14.34[c]$\pm$0.38	4.89[b]$\pm$0.40	0.25[a]$\pm$0.02

*Values in the same column containing the same superscript are not significantly different from each other (Fisher test, $p < 0.05$)

Fig. 2 Tensile strength of TPS/PP (70/30) blends: (**a**) control blends without acid (CONTROL); (**b**) corn blends, (**c**) potato blends and (**d**) cassava blends
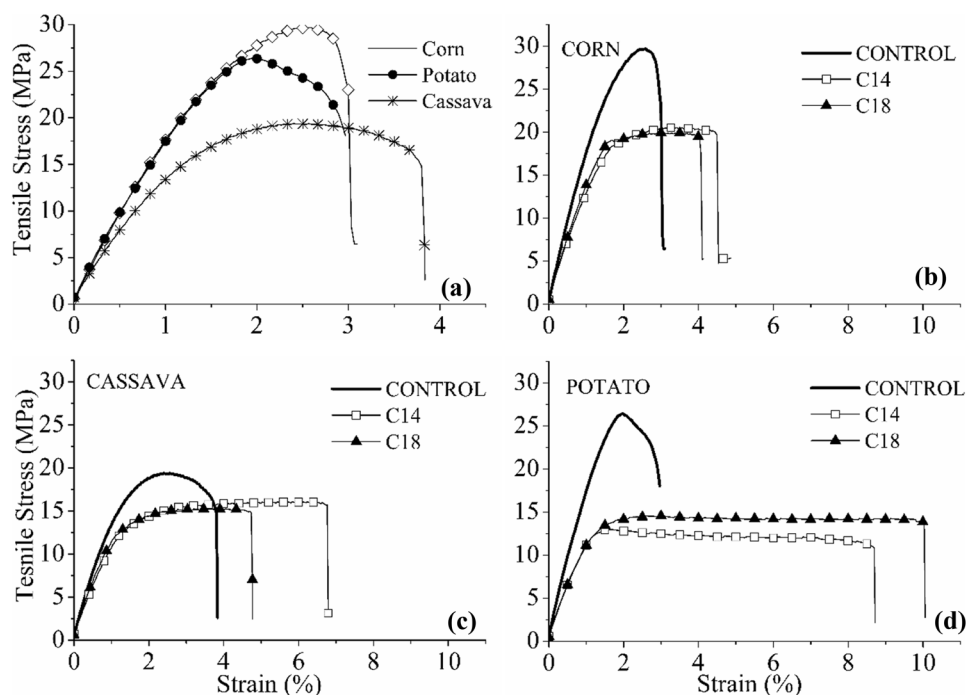

Regarding the influence of acid type on tensile properties, for corn blends data indicates no significant difference between tested acids ($p > 0.05$). However, for potato and cassava blends, the acid type had a significant influence ($p < 0.05$). An hypothesis for this behaviour is related to the fact that cereal starches (as corn) contain lipids in the native granule, whereas tuber starches (as potato and cassava) are virtually lipid free [45]. So, it may improve its amylose capability to form those complexes with the added acids, affecting the mechanical properties. However, for cassava starch blends with C14 showed better results than ones with C18, whereas for potato starch blends, blends with C18 showed better results. The higher elongation at break for potato C18 blends can be attributed to the higher hydrophobic of longer carbon chains and the resulting stronger interaction within the hydrophobic helix cavity and higher ultimate strain.

Influence of starch source and acid incorporation on the morphological properties of TPS/PP (70/30) blends.

Images of TPS/PP (70/30) impact-fractured surface obtained by SEM are illustrated in Fig. 3. From the blends morphology without acid (control) (Fig. 3a, 4a and 5a), it was possible to note a co-continuous morphology, where neither of the blend phases can be defined as the matrix or the dispersed phase. Mazerolles et al. [46] also observed a co-continuous morphology for TPS/LDPE (70/30) blends. It can be seen the presence of two distinct phases: a fragile fracture surface, without apparent plastic deformation, which was attributed to the polypropylene; and a ductile fracture surface, without roughness, which was attributed to the gelatinized starch granules. The boundaries between them are clear and there are cavities (or gaps). Furthermore, coalescence of gelatinized starch granules and poor dispersion of both phases were observed, probably it was due to the polymer's immiscibility. This incompatibility is associated to the chemical difference of components and was also reported by [17, 47, 48].

Fig. 3 SEM micrographs of impact-fractured surface for TPS/PP (70/30): CORN blends: (**a**) control (without acid); (**b**) with 3% C14 and (**c**) with 3% C18
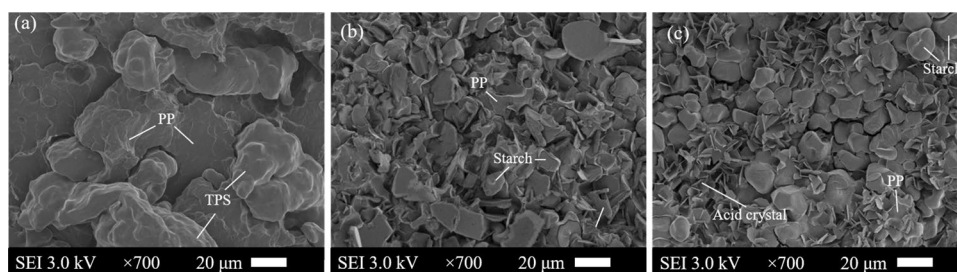
Fig. 4 SEM micrographs of impact-fractured surface for TPS/PP (70/30): for POTATO blends (**a**) control (without acid); (**b**) with 3% C14 and (**c**) with 3% C18
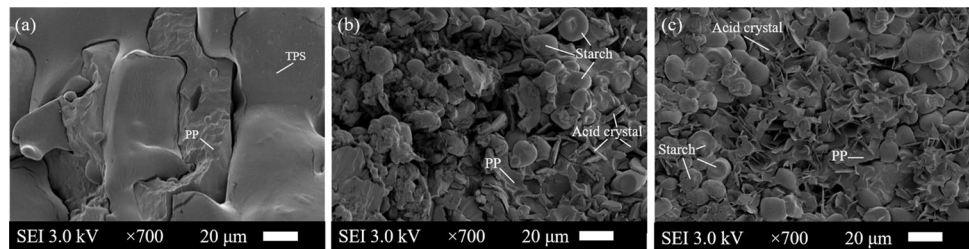
Although we expected a complete gelatinization of starch, SEM images of acid-blends (Fig. 3b-c, 4b-c and 5b-c) exhibited starches granular structures and phase separation. SEM images presented a typical droplet-in-matrix morphology, where many granular particles were observed, indicating an increase of affinity between starch and PP. This implies that, although in large quantity (70%), TPS was not fully destroyed and the regular starch morphology could be seen disperse on PP phase. Starch has a granular structure, when it is heated under a certain temperature and in the presence of a plasticizing, its granular structure is disrupted in the gelatinization process, giving rise to the thermoplastic starch [49]. This said, in the Fig. 3a, 4a and 5a (blends without acid) starch was gelatinized and a homogeneous morphology could be seen. While, in SEM images of blends with acid the granular structure remained and a great dispersion was observed. Raphaelides et al. [42] also observed the presence of intact granules in the fatty acid containing samples. They attributed this phenomenon to granules reinforcement, by the amylose–lipid complexes on their surface. Perhaps it could explain the presence of a membrane-like structure around the fractured potato granules on acid-blends. SEM images. On the other hand, in the case of cassava acid-blends, an improve on impact resistance could be related to self-reinforcing properties of granular structure [38] combining to compatibilizer effect of acids.

On Fig. 3b and 3c, a polygonal shape, typical of corn starch, is noted. On Fig. 4b and 3c, an elliptical structure typical of potato starch is noted, with the biggest granule diameter. On Fig. 5b and 5c, a spherical structure typical of cassava starch is noted. Since shape and granule size depends on starch botanical origin, these findings are in accordance to one found by [11].
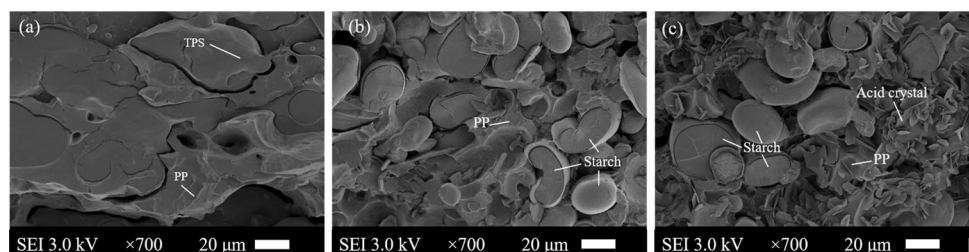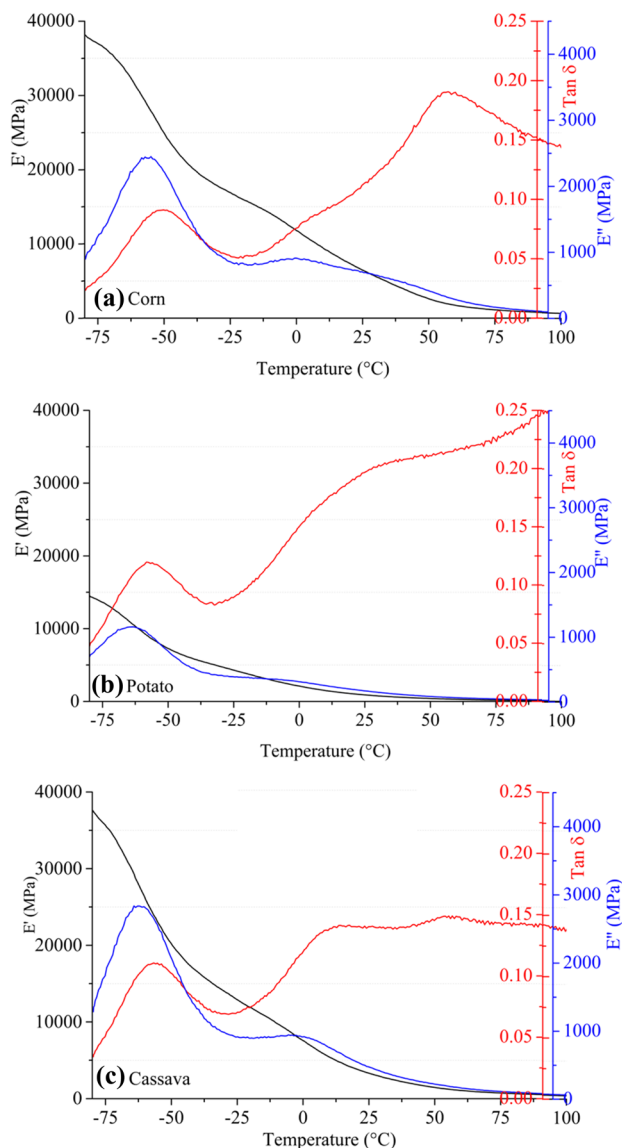
It was possible to note that on SEM images of acid-blends (Fig. 3b-c, 4b-c and 5b-c) an amount of crystal-like structures was randomly dispersed in PP phase, which indicates that these acids also have good compatibility with PP. In this sense, C14 crystals were flatter, in contrast to the C18 structure, which tended to be needle-like. This morphology is consistent with the crystal polymorphs of carboxylic acids that possess carbon chain lengths of C10 to C20 [50]. Besides, it was possible to note on SEM images that blends with C18 (Fig. 3c, Fig. 4c and Fig. 5c) presented a greater quantity of crystals, than blends with C14 (Fig. 3b, Fig. 4b and Fig. 5b). This behavior was not starch type dependent. It can indicate that C14 can make greater intermolecular interaction with PP/starch molecules, giving raise to blends with better mechanical performance. Probably because of its smaller carbon tail, myristic acid can interact more effectively than stearic acid.

Influence of starch source and acid incorporation on the dynamic-mechanical properties of TPS/PP (70/30) blends.

Figure 6a shows the curves of the storage modulus (E'), loss modulus (E'') and tan δ for control blends according to starch source. The glass transition temperature (Tg) was detected at the sharp decrease in E' and the peak of curves corresponding of loss of E'' or tan δ. The Tg value obtained from the tan δ peak was several degrees higher than that from the peak in E''. In this respect, the Tg values were based on the E'' peak as it is regarded as the most appropriate value [51]. TPS/PP blends exhibited two peaks of glass transition temperatures (Tg): the upper transition (T_α) is characteristic of starch-rich phase on TPS, while the lower one is associated to the glycerol-rich domains (T_β)[52–55]. Regarding corn control blends, T_α and T_β occurred at +2.17 and -54.24 °C, whereas for potato control blends it occurred at +0.72 and -62.77 °C and for cassava control blends at +0.45 and -61.98 °C, respectively.

Fig. 5 SEM micrographs of impact-fractured surface for TPS/PP (70/30): for CASSAVA blends (**a**) control (without acid); (**b**) with 3% C14 and (**c**) with 3% C18

Fig. 6 Storage Modulus, E'; Loss modulus, E'' and tan δ of TPS/PP (70/30) control blends: (**a**) corn starch blends (**b**) potato starch blend and (**c**) cassava starch blend

A decrease of E' with increasing temperature was observed in all samples as an effect of the softening of materials at higher temperatures. A gradual decrease is related with semicrystalline polymers. Among starch sources, potato starch blends presented lower storage modulus values. Beyond the T_α, only for potato control blends a plateau can be seen where the modulus decreases slowing. Once it depends on the crystallinity index, DSC analysis were made and the thermograms are presented in Fig. 7.

Potato control blends presented the higher crystallinity among blends, which can be related to its higher amylose content and justifies the presence of the plateau on Fig. 6b. As mentioned before, during retrogradation process, the
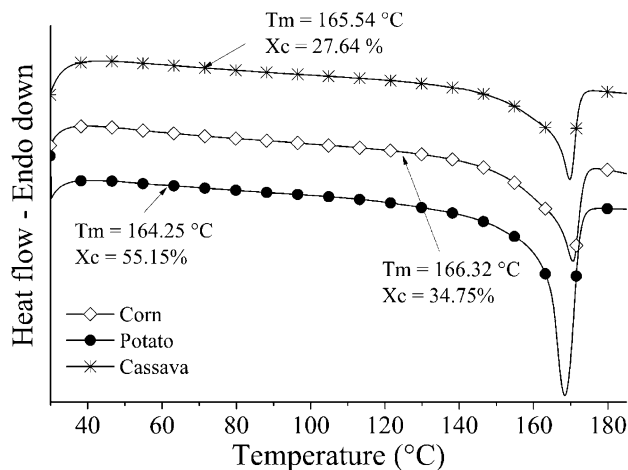
Fig. 7 DSC thermograms of TPS/PP (70/30) control blends

reassociation of long linear amylose chain happens, increasing crystallinity.

With the intention of studying the behaviour of acid addition, Fig. 8 presents the E'' of all TPS/PP blends.
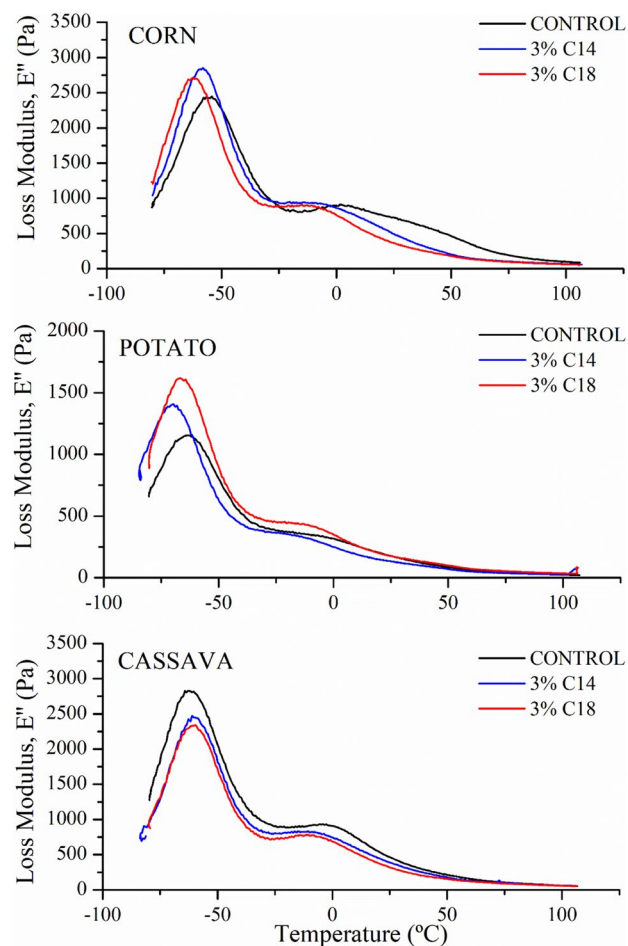
Fig. 8 Loss modulus, E'' of TPS/PP (70/30) blends

Table 2 Glass transition temperatures (Tg) of all studied TPS/PP (70/30) blends, were T_α is the upper transition and T_β is the lower transition

Starch		T_β (°C)	T_α (°C)
CORN	Control	-54.24	+2.17
	C14	-58.06	-4.60
	C18	-62.58	-7.78
POTATO	Control	-62.77	+0.72
	C14	-69.61	-13.94
	C18	-66.66	-7.93
CASSAVA	Control	-61.98	+0.45
	C14	-58.69	-7.59
	C18	-59.61	-7.95

It was possible to note a Tg peak temperature displacement, after acid incorporation. For corn and potato blends with acid both peaks were dislocated to the left and were located below the value obtained for control blends, indicating a more plasticizer effect. However, for cassava blends peaks had dislocated on the direction of each other (Table 2). This can be interpreted as compatibilizer effect of the carboxylic acids. Taguet et al.[56] also showed that compatibilizer insertion influenced the position of glycerol-rich phase peak. These results provide more evidences that, for cassava blends, acids acted as a compatibilizer, whereas to others blends acids acted as a plasticizer.

Influence of starch source into TPS/PP (70/30) blends processing.

Torque curves as function of time and the specific mechanical energy (SME) of TPS/PP (70/30) are shown on Fig. 9 and Fig. 10, respectively. The torque data from blends without acids (control) indicates that the maximum torque was smaller for cassava when compared to corn and potato starch, which values correspond to 13.5, 21.6 and 21.2 Nm, respectively. SME values ranged from 320 to 435 kJ/kg. The corn-control blends showed the highest values, followed by the potato-control blends with 378 kJ/kg. and cassava-control blends with the smaller one. These results can indirectly correlate with the molar mass, since a high torque is influenced by a higher viscosity. The high SME value reached during corn and potato starch processing was attributed to their higher amylose content, 23.08 and 24.73% respectively, compared to cassava starch with 20.39%.

Nevertheless, adding acids decreased torque maximum values and consequently the SME energy. In addition, an increase on the time to torque peak, in other words, the torque peak shifts to the right when C14 and C18 were added. This phenomenon can be explained by the lubricant effect of acids. That makes the mass less resistant to rotor friction, until a certain point where acid will be incorporate into the mass. Stearic acid was also used as processing aid agent as report by [57].

Among starches, potato starch blends seem to be more susceptible to acid incorporation, as torque decreased from 21.6 Nm to 9.8 Nm by C18 addition. This behavior was attributed to the higher phosphorus content on potato starch [39, 58]. Castaño et al.[4] demonstrated that phosphorus content influences starch plasticization in shear, where the repulsion between phosphate groups facilities the diffusion

Fig. 9 Torque curves of TPS/PP (70/30) blends: (**a**) control blends without acid (CONTROL); (**b**) corn blends, (**c**) potato blends and (**d**) cassava blends
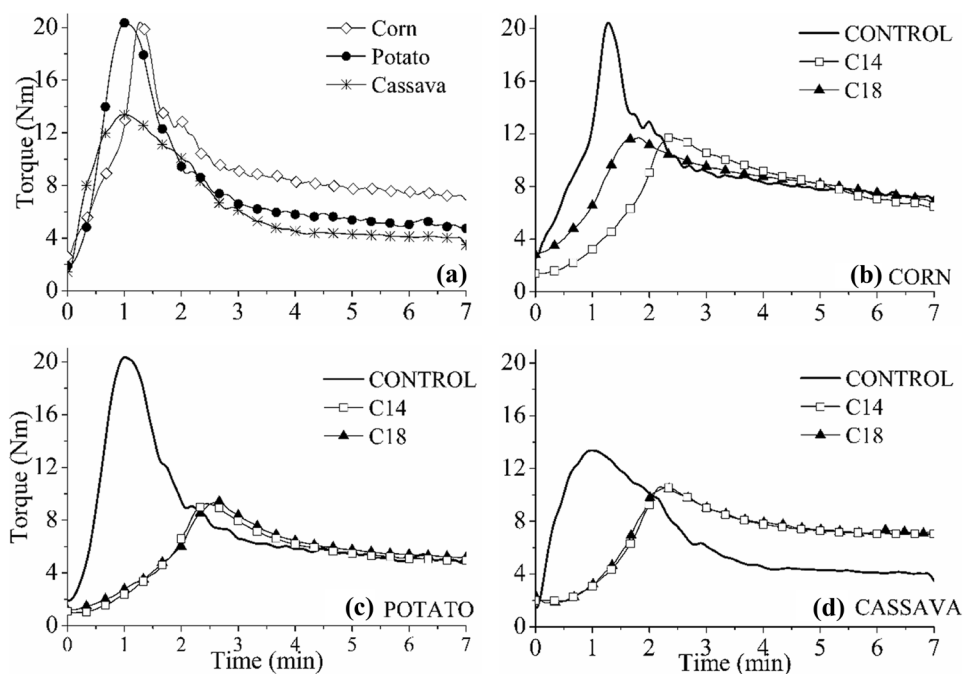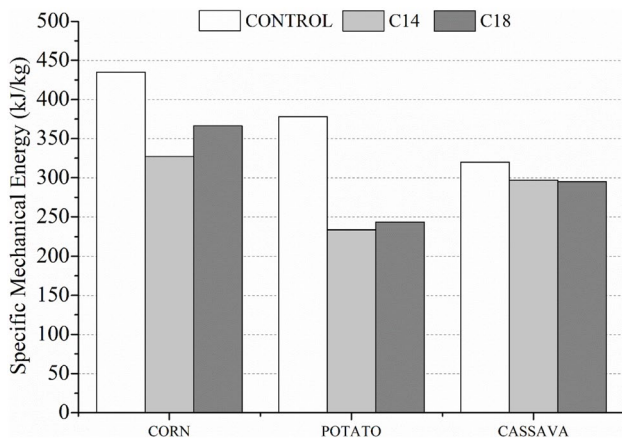
Fig. 10 Specific mechanical energy (SME) of TPS/PP (70/30) blends according to starch source for blends without acid (CONTROL), with myristic acid (C14) and stearic acid (C18)

of plasticizer into starch chains, changing starch-paste viscosity. Probably, this effect also explains the higher elongation at break values for potato blends with C18 (Table 1) rather than C14, once stearic acid (C18) has higher molar mass.

Relating the morphology and the SME, it can be inferred that a minimum of energy is necessary to lead to starch coalescence. Since, for control blends SME was higher than 300 kJ/kg and starch was gelatinized. However, for blends with acids, less quantity of energy was consumed and the starch maintained its granule structure. These results corroborated the literature data, where is possible perceive that a higher torque is required for destruction/melting of starch particles [4]. Also, as already discussed, acids act also as aid processing agent, lowing the shear stresses, which might be not enough to destroy the starch granules.

Conclusions

In this study, starch/polypropylene (70/30) blends with distinct starches (corn, potato and cassava) were produced. Two carboxylic acids were used (myristic and stearic acids) to improve blends properties. For control blends (without acid), the starch source had no influence on the impact strength properties. However, when acids were used, impact strength differed significantly from starch source and acid type, where cassava blends with myristic acid showed the best results. It was found that the plasticization was potentiated by the presence of acids due to the formation of amylose–lipid complexes, rendering samples with lower elastic modulus and tensile strength, but greater elongation at break. Potato starch blends with C18 obtained higher values for deformation at break, demonstrating a greater plasticizing effect for

this acid. Torque reduction and Tg displacement were also observed for blends with acid. From SEM images, different morphologies could be seen, where control blends (without acid) showed a co-continuous morphology and weak interfacial adhesion. Whereas acid-blends showed a droplet-in morphology with better granules dispersion where starch gelatinization did not occur. Results suggested that carboxylic acids act differently according to the starch source.

Compliance with ethical standards

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